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June 23, 1999

John DaMassa
Planning and Technical Support Division
California Air Resources Board
2020 L Street
Sacramento, CA 95814

Re: Review of Organic Gas Speciation Profiles of Exhaust and Evaporative Emissions from Alternate Gasoline Formulations

Dear John:

I have reviewed the speciation profiles that Paul Allen sent via E-mail on June 8, and am providing my comments and analysis of these profiles to you in this letter. Separate sets of speciation profiles were provided corresponding to 4 different gasoline formulations. Each of the profiles is identified by profile number; these profile numbers will be used in the comments that follow. Note that any changes to base profiles for RFG with 2% oxygen from MTBE will also affect the profiles for other fuels, since they were obtained by adjusting the base (MTBE) profiles.

	MTBE @ 2%	Ethanol @ 2%	Ethanol @ 3.5%	RFG without oxygenates
Liquid fuel	419	660	670	650
Diurnal evap.	906	661	671	651
Hot soak evap.	420	662	672	652
Catalyst exhaust stabilized	876	663	673	653
Catalyst exhaust starts	877	664	674	654
Non-cat exhaust stabilized	401	665	675	655
Non-cat exhaust starts	402	666	676	656

DISCLAIMER: Given the time available to complete my review, and the complexity of the information provided, it was not possible to review the values specified for all chemical species in each profile. I have emphasized in my review 16-20 of the most abundant species in unburned fuel and exhaust emissions, as well as formaldehyde, acetaldehyde, benzene, and 1,3-butadiene. My review identifies some areas where further consideration of the profiles by ARB staff is recommended; I leave it to ARB staff to decide in the end whether the profiles are correct and appropriate for use in air quality modeling.

SUMMARY OF COMMENTS:

Here I identify the most important issues recommended for further consideration, ranked subjectively in terms of how revisions may affect the assessment of ozone formation and air toxic concentrations in subsequent air quality modeling.

- There are numerous problems with the hot soak profiles for all 4 fuels:
  - there appear to be duplicate entries for ethyltoluene isomers.
  - the benzene content varies much more widely in the hot soak profiles than it does in the fuels. Furthermore, variations in hot soak benzene content do not agree with benzene changes in liquid fuel composition.
  - the composition of hot soak emissions does not appear to be well-correlated to the liquid fuel composition for other species including toluene, m-xylene, and 2,2,4-trimethylpentane.

- The benzene content of diurnal emissions appears low given the assumed benzene levels in liquid gasoline; variations in benzene content in diurnal emissions across fuels are not consistent with changes in fuel composition.

- The oxygenate content in exhaust emissions profiles may be too low, especially for ethanol but also MTBE to a lesser degree.

- Acetaldehyde emissions are expected to increase when ethanol is added to gasoline. Further increases are expected when ethanol content is increased from 2 to 3.5% oxygen, yet all of the exhaust profiles are nearly identical in acetaldehyde content when ethanol increases from 2 to 3.5% oxygen in the fuel.

- The ethanol content in diurnal evaporative emissions (profiles 661 and 671) may not scale linearly with fuel ethanol content, due to non-ideal solution behavior.

- Isobutene content in exhaust profiles 653 and 655 looks high for gasoline without oxygenates.

- Butadiene emissions may increase in exhaust profiles 653-656 if the olefin content of the fuel increases.

- The methane content in catalyst-equipped stabilized engine exhaust in 1996 appears high compared to on-road data.

- Acetylene in non-catalyst stabilized exhaust profiles is too low.

More detailed comments, tables and figures, are attached. Please call me at (510) 643-9168 if you have any questions. I hope these comments are useful to you in your assessment of various alternate gasoline formulations.

Sincerely,

Rob Harley

Robert Harley
Associate Professor

DETAILED COMMENTS: Review of Organic Gas Speciation Profiles of Exhaust and Evaporative Emissions from Alternate Gasoline Formulations.

Comment 1: CAT STABILIZED EXHAUST PROFILE FOR RFG w/MTBE. The stabilized exhaust profile for catalyst-equipped engines (profile 876) is compared in the attached Figure 1 with the on-road running emissions profile measured in the Caldecott tunnel in summer 1996 for 20 individual species that together account for >70% of non-methane organic compound emissions in profile 876 and in the tunnel. The tunnel profile is similar to profile 876 for all species except MTBE, which accounted for 5.0% of tunnel VOC (5.5% of tunnel NMOC), whereas profile 876 includes only 2.0% by weight MTBE. Methane is not shown in Figure 1; it accounted for 15.8% of VOC in profile 876 versus 9.1% of VOC in the Caldecott tunnel. A 1996 emissions-weighted average of the profiles for cat and non-cat stabilized exhaust should give around 10% methane to agree with on-road data.

Comment 2: CAT STABILIZED EXHAUST PROFILES FOR ALL 4 FUELS. The stabilized exhaust profiles for all 4 fuels for catalyst-equipped engines (profiles 876, 663, 673, and 653) are compared for selected species in Figure 2. Abundances of species shown in Figure 2 are similar across all profiles, except for five species shown at the right: isobutene, formaldehyde (HCHO), acetaldehyde (CCHO), MTBE, and ethanol. Changes for these species are expected if changes are made in gasoline oxygenate content.

While addition of MTBE to gasoline is expected to lead to increased emissions of isobutene in vehicle exhaust (Hoekman, 1992; Kirchstetter et al., 1999), further consideration should be given as to whether isobutene would increase as much as shown in Figure 2 when switching from RFG containing ethanol to RFG without any oxygenate.

Given that ethanol accounts for 5.75 and 10.1% of gasoline mass (these values correspond to 2 and 3.5% by weight oxygen, respectively), it is surprising in profiles 663 and 673 that ethanol accounts for only 0.25 and 0.5% of exhaust VOC mass. I would predict that roughly half of the exhaust would be unburned fuel, and so would expect as much as an order of magnitude higher ethanol (3-5%) in exhaust emissions depending on fuel ethanol content. Further consideration of this issue is recommended.

Comment 3: EXHAUST PROFILES FOR RFG w/MTBE. For gasoline containing 2% oxygen as MTBE, a comparison of exhaust profiles for catalyst/non-catalyst engines and stabilized/start emissions is presented in Figure 3. Isopentane is higher in the stabilized profiles than in the start profiles. Aromatics (toluene, ethylbenzene, xylenes, and 1,2,4-trimethylbenzene) are less abundant in the catalyst stabilized exhaust profile (876) when compared to the other profiles shown in Figure 3. Acetylene in the non-catalyst stabilized exhaust profile (401) is the lowest of all profiles shown in Figure 3, which is unexpected because vehicles with catalytic converters are expected to have the lower acetylene levels. ARB staff should consider specifying a higher acetylene fraction in profile 401. I am concerned that using the highest-emitting vehicles from ARB in-use surveillance testing may not accurately represent non-catalyst engine emissions.

Comment 4: LIQUID FUEL. In Figures 4 and 5, liquid fuel composition in profile 419 is compared against measured fuel composition in the SF Bay Area from summer 1996 (Kirchstetter et al., 1999). The profiles are similiar in terms of distribution of species across organic compound categories (Figure 4) and for the top 16 identified species listed in profile 419 (Figure 5). These 16 species account for >60% of the mass in profile 419. Profile 419 seems reasonable in comparison to the liquid fuel data from the Bay Area, although differences exist in the specific isomers and types of alkanes present. Further comparisons of profile 419 against Los Angeles area gasoline composition measured during summer 1996 (Norbeck et al., 1998) could be helpful.

Comment 5: HOT SOAK. Duplicate entries exist in the hot soak emission profile (420) for all 3 isomers of ethyltoluene (also called methyl-ethyl-benzene). ARB staff should consider deleting the entries for SAROAD codes 45211, 45212, and 98164 in profile 420, which duplicate entries for SAROAD codes 99915, 99912, and 99914, respectively. If this change is made, the profile will need to be renormalized to sum to 100%, and the hot soak profiles for other fuels (numbers 652, 662, and 672) should be rederived based on the revised profile 420.

The benzene content in hot soak emissions varies widely across fuels, from a low of 3.3% to a high of 4.9% by weight. Given the modest changes specified in fuel benzene content, the changes appear too large, and furthermore the highest hot soak benzene content is specified for the liquid fuel having the lowest benzene (profile 652). A large decrease in hot soak benzene occurs between profiles 662 and 672, while fuel benzene hardly changes.

The composition of hot soak evaporative emissions may approach, in some cases, the composition of liquid gasoline, especially for older vehicles with carburetors. Large differences exist in the relative abundances of toluene (15.1% in profile 420 vs. 6.7% in liquid fuel), m-xylene (8.8% in profile 420 vs. 3.5% in liquid fuel), and 2,2,4-trimethyl-pentane (2.1% in profile 420 vs. 5.5% in liquid fuel).

Comment 6: DIURNAL. A gasoline headspace vapor profile (906) is used to represent the speciation of diurnal evaporative emissions. This profile was derived using vapor-liquid equilibrium theory and measured composition of liquid gasoline from the Bay Area in summer 1996 (see Kirchstetter et al., 1999). This profile is likely to describe the compostion of displaced gasoline vapor emissions that occur during refueling (Furey and Nagel, 1986). For diurnal emissions from vehicles equipped with correctly-functioning activated carbon canister control systems, other factors such as differing uptake rates of individual VOC, canister carryover effects, and permeation of VOC through fuel system elastomers, can affect VOC composition (Urbanic et al., 1989; Burns et al., 1992). Therefore, an equilibrium headspace vapor composition profile may not represent all diurnal evaporative emissions correctly. Also the benzene levels in profile 906 were calculated from Bay Area liquid gasoline composition which included 0.58% benzene, as opposed to 1.00 wt% benzene in profile 419 (unburned fuel profile, RFG w/MTBE). Therefore profile 906 is likely to understate the benzene content of diurnal evaporative emissions relative to what is specified in the liquid fuel in profile 419.

The level of benzene in diurnal profile 651 (0.52% for RFG w/o oxygenate) is not consistent with benzene content in the liquid fuel, which is the lowest of all 4 fuels, whereas the corresponding diurnal profile has the highest benzene value.

The presence of ethanol in headspace vapor/diurnal evaporative emissions may not scale linearly with ethanol content in fuel, because ethanol exhibits non-ideal behavior in solution with non-polar gasoline hydrocarbons (Bennett et al., 1993), and the activity coefficient increases as ethanol content decreases. Therefore, decreases in ethanol in the liquid may be offset in part by increases in its activity coefficient. Further analysis of profiles 661 and 671 is recommended.

ARB staff should move isomers of ethyltoluene listed in the diurnal evap profiles to list them under SAROAD codes 99915, 99912, and 99914, for consistent labeling of these species across all 7 profiles for each fuel.

Comment 7: BUTADIENE. 1,3-butadiene is present in exhaust emissions, but is not present in any of the evaporative emissions profiles supplied by ARB. This is appropriate. At present there are only minor differences in butadiene weight fractions across the different fuels. Increases in olefin content in unburned fuel may increase butadiene emissions in vehicle exhaust (e.g., Table 3 of Gorse et al., 1991). Therefore, ARB staff should consider whether converting 80% of butane content to butene to construct profile 650 would lead to increased butadiene in the exhaust profiles for gasoline without oxygenate.

Comment 8: ACETALDEHYDE. Profiles 673-676 correspond to exhaust emissions for gasoline with 3.5% oxygen as ethanol. Given the higher fuel ethanol levels, emissions of acetaldehyde should increase compared to profiles 663-666 where ethanol is present at only 2% oxygen, yet the profiles are virtually identical in terms of acetaldehyde content.

Comment 9: OTHER. There are errors in the molecular weights assigned to some of the chemical species in the speciation profiles that were sent to me. Recommended corrections are listed in the attached Table 1. Depending on the chemical mechanism and emission processing procedures used in air quality modeling, these errors in molecular weights could affect conversion of emission rates from mass to molar units. Also, in estimating headspace vapor composition from liquid fuel composition, accurate molecular weights are needed to convert between mass fractions and mol fractions. The most important change is likely methylcyclohexane (43261) where the molecular weight should be 98.2 rather than 85.2 g mol^{-1}.

REFERENCES:

Bennett, A.; Lamm, S.; Orbey, H.; Sandler, S.I. (1993). Vapor-liquid equilibria of hydrocarbons and fuel oxygenates. 2. *Journal of Chemical Engineering Data* **38**, 263-269.

Burns, V.R.; Reuter, R.M.; Benson, J.D.; Gorse, R.A.; Hochhauser, A.M.; Koehl, W.J.; Painter, L.J. (1992). Effects of gasoline composition on evaporative and running loss emissions — Auto/Oil Air Quality Improvement Research Program. *SAE Technical Paper Series*, no. 920323.

Furey, R.L.; Nagel, B.E. (1986). Composition of vapor emitted from a vehicle gasoline tank during refueling. *SAE Technical Paper Series*, no. 860086.

Gorse, R.A.; Benson, J.D.; Burns, V.R.; Hochhauser, A.M.; Koehl, W.J.; Painter, L.J.; Reuter, R.M.; Rippon, B.H. (1991). *SAE Technical Paper Series*, no. 912324.

Hoekman, S.K. (1992). Speciated measurements and calculated reactivities of vehicle exhaust emissions from conventional and reformulated gasolines. *Environmental Science & Technology* **26**, 1206-1216.

Kirchstetter, T.W.; Singer, B.C.; Harley, R.A.; Kendall, G.R.; Hesson, J.M. (1999). Impact of California reformulated gasoline on motor vehicle emissions: 2. Volatile organic compound speciation and reactivity. *Environmental Science & Technology* **33**, 329-336.

Norbeck, J.M.; Sodemann, S.P.; Miguel, A.H. (1998). Baseline gasoline composition study. CE-CERT, University of California, Riverside, CA. Final report to the South Coast Air Quality Management District, contract no. C94166-2.

REFERENCES (continued):

Urbanic, J.E. (1989). Effect of humid purge air on the performance of commercial activated carbons used for evaporative emissions control. *SAE Technical Paper Series*, no. 892039.

TABLE 1: Recommended Changes to Molecular Weights for Individual VOC

SAROAD:	Species Name:	Molecular Weight:
99912	m-ethyltoluene	120.19
99914	p-ethyltoluene	120.19
99915	o-ethyltoluene	120.19
98179	1-ethyl-2-n-propylbenzene	148.25
45250	isomer of dimethylethylbenzene	134.22
45251	"	"
45252	"	"
45254	"	"
45257	"	"
91099	"	"
45256	1-(1,1-dme)-3,5-dimethylbenzene	162.26
91115	t-1-butyl-3,5-dimethylbenzene	162.26
91117	1,3,5-triethylbenzene	162.26
91119	1,2,4-triethylbenzene	162.26
46751	dihydronaphthalene	130.19
91122	pentamethylbenzene	148.23
43261	methylcyclohexane	98.18
90116	propylcylopentane	112.21
91057	trimethylcyclohexane isomer	126.24
91061	"	"
91064	"	"
91066	"	"
91074	"	"
91077	butylcyclopentane	"
91085	"	"
91067	2-methyl-1-octene	126.24
91080	trans-3-nonene	126.24
91084	cis-3-nonene	126.24
43222	1,3-butadiyne	50.06
91097	ethylnonane	156.3

Figure 1: Comparison of Stabilized Exhaust Profile 876 with On-Road Emissions Profile (1996 Caldecott tunnel)

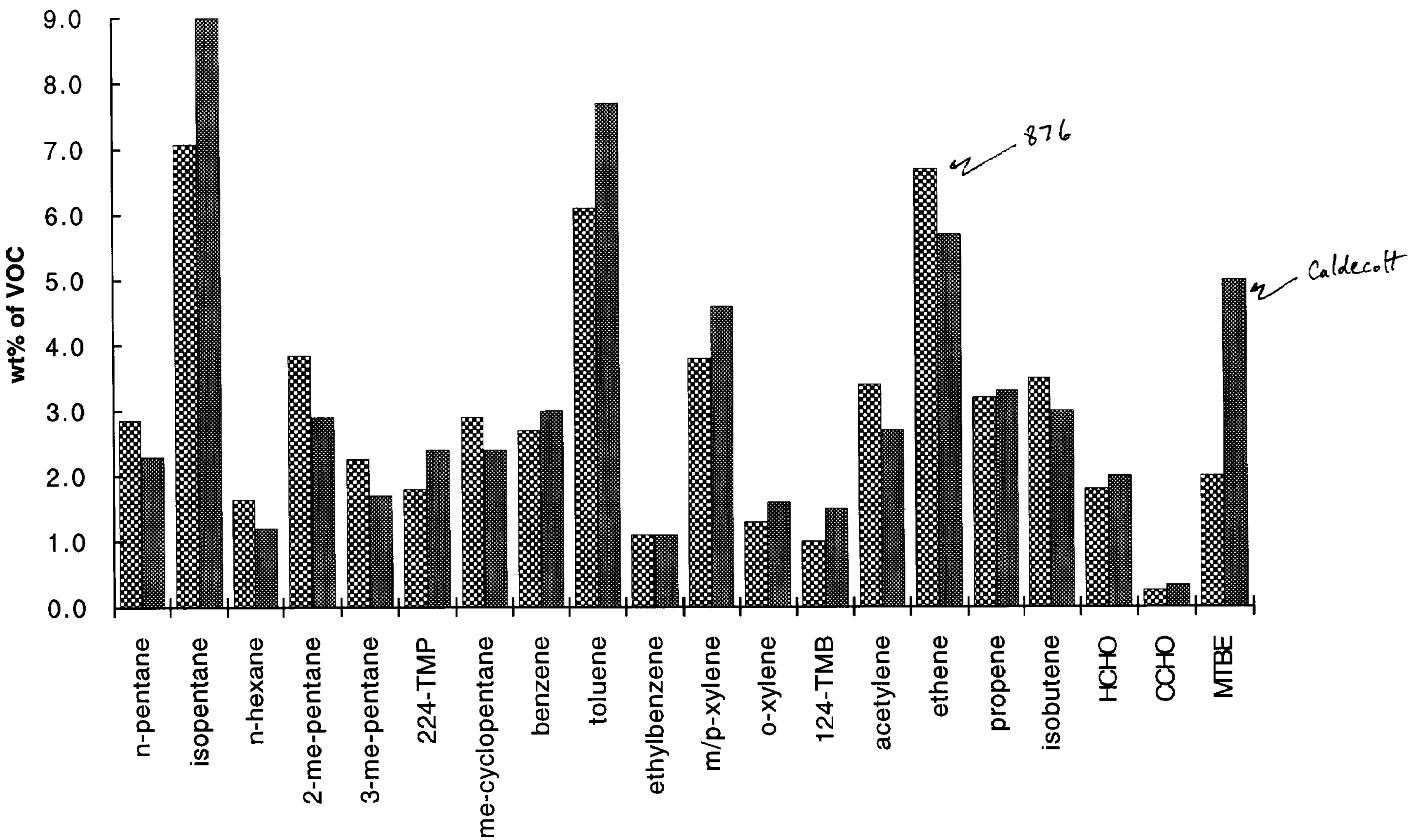

Figure 2: Comparison of Stabilized Exhaust Profiles for RFG with MTBE (876), 2% as ETOH (663), 3.5% as ETOH (673), and w/o oxy (653), in that order

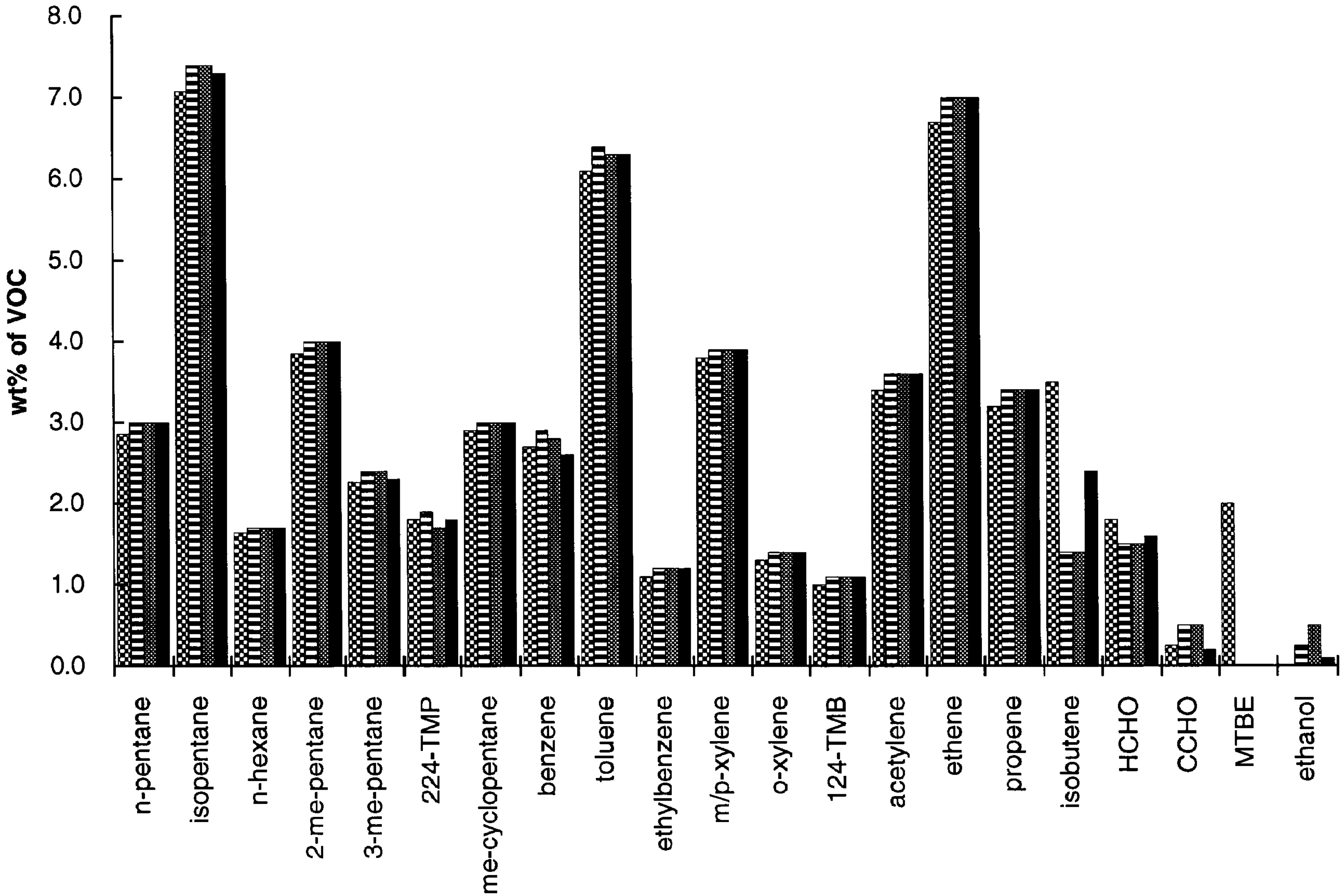

Figure 3: Comparison of Exhaust Speciation Profiles for RFG with MTBE (Profiles are CAT STAB, CAT STRT, NON-CAT STAB, and NON-CAT STRT in that order)

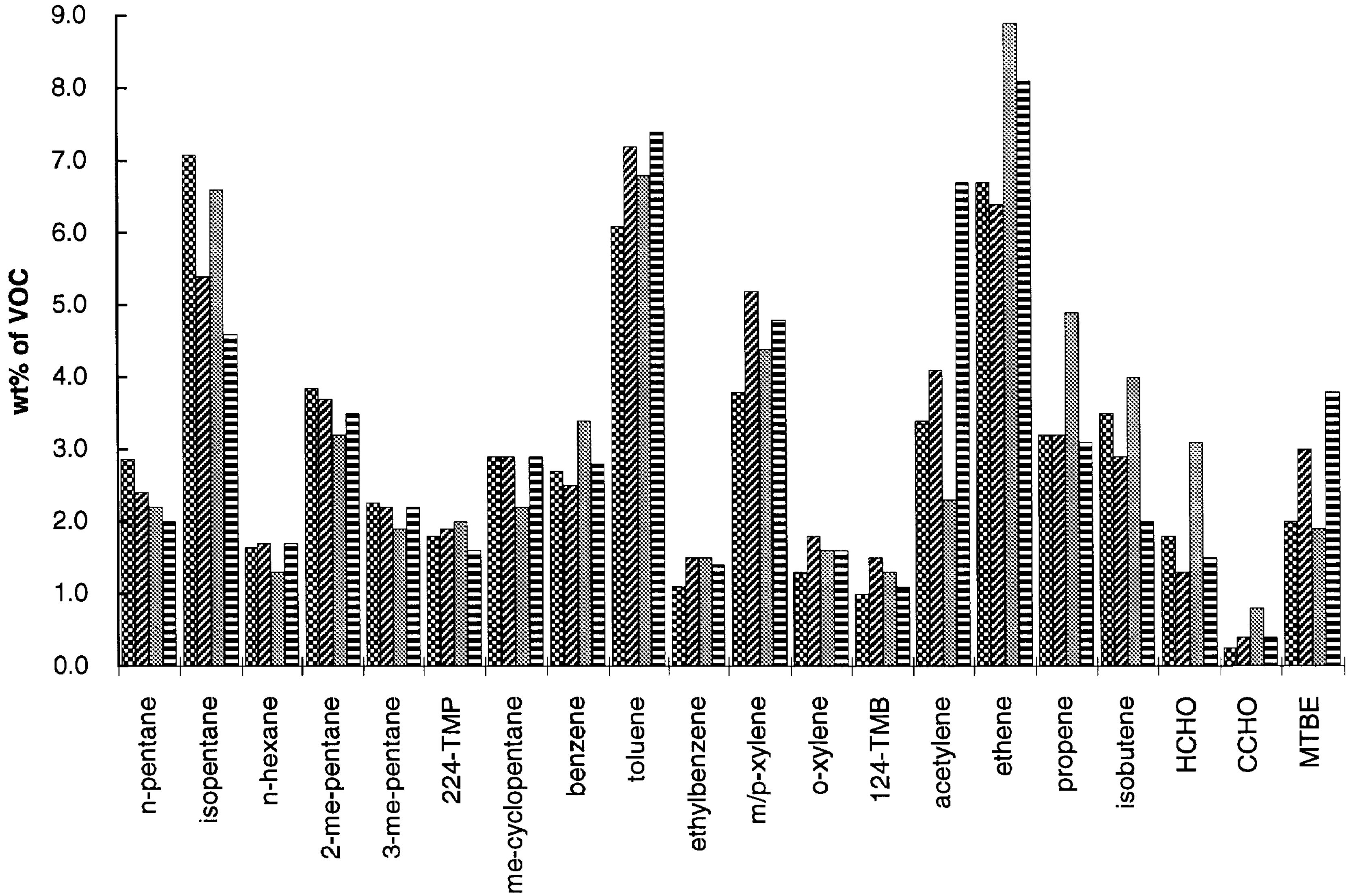

Figure 4: Comparison of Gasoline Composition, Profile 419 (left bars) vs. Bay Area Summer 1996 Composite (right bars)

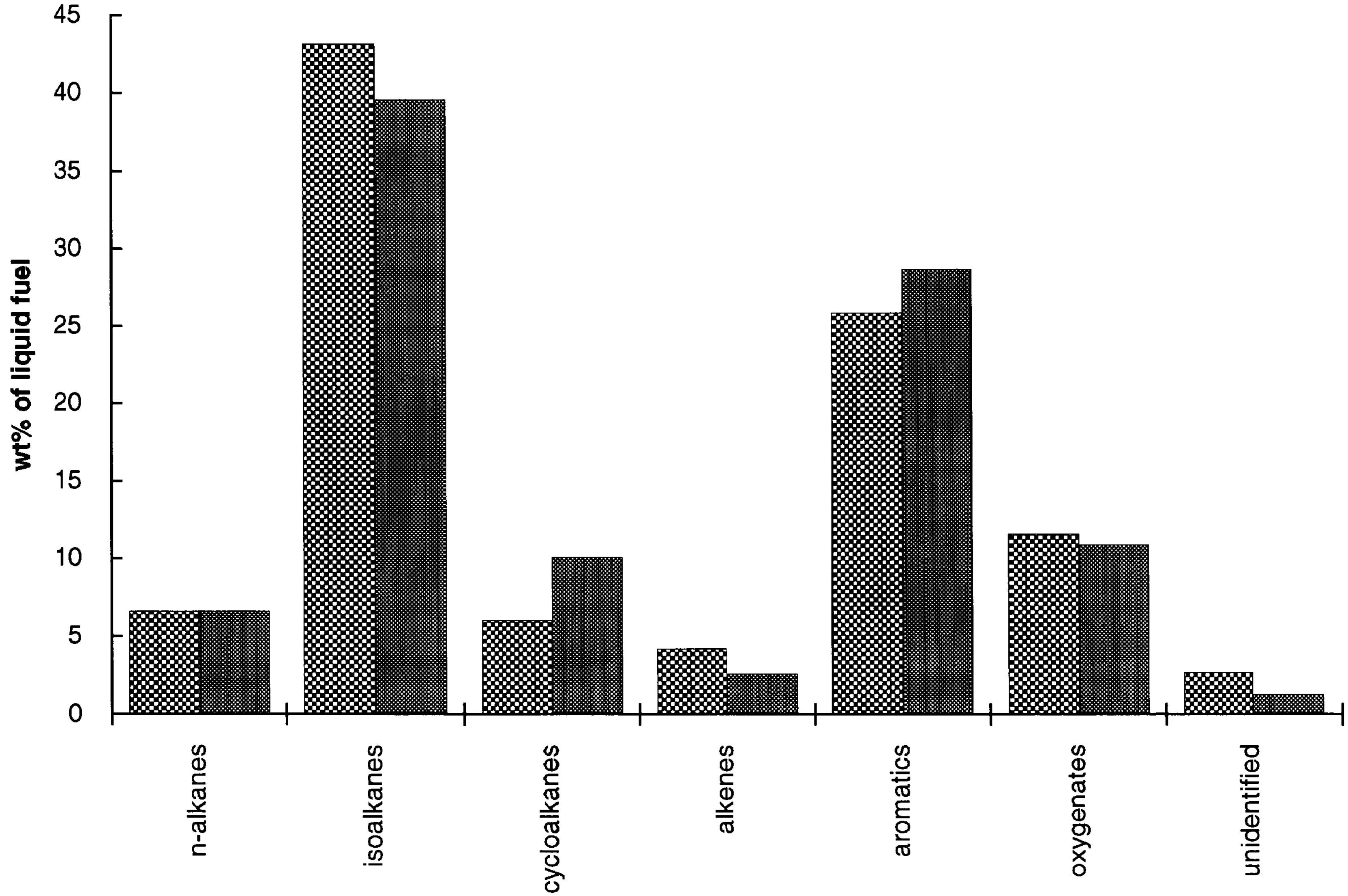

Figure 5: Comparison of Gasoline Composition, Profile 419 (left bars) vs. Bay Area Summer 1996 Composite (right bars)